

Characterization of Solvent Refined Coal by High Pressure Liquid Chromatography and other Analytical Techniques

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Solvent Refined Coal (SRC) has previously been investigated by gel permeation chromatography (GPC)(1-3) and open column liquid chromatography (4,5). These studies have concentrated on comparison among various untreated coals and SRC's along with the determination of classes of chemical compounds present in SRC. In this paper the basic chemical nature of SRC is investigated, both on a molecular size basis and on a component basis.

By determining the basic chemical characteristics of SRC, important ground work can be laid for understanding the structure of SRC and for a fundamental understanding of the parent coal. Through knowledge of the molecular size distribution of SRC it may be possible to determine the process parameters which control the product composition. Knowledge of the chemical entities composing SRC, should make it possible to better structure the process so as to enhance product quality.

To provide a better understanding of the chemical makeup of SRC, this work presents an in-depth study of its chemical characteristics. SRC is analyzed at three different separation levels: 1) initially, the THF soluble portion of SRC is analyzed by GPC and the molecular size distribution is obtained; 2) GPC is used as a preanalysis step in which individual fractions are collected according to their elution time for subsequent detailed analysis; and 3) the SRC fractions are separated into component peaks or chromatographic bands by high pressure liquid chromatography (HPLC) and gas chromatography (GC).

Experimental

Materials Studied

Four SRC's, Amax, Western Kentucky 9/14, Monterey and Illinois #6, and their respective feed coals were obtained from the Wilsonville SRC Pilot Plant. The light recycle oil was obtained from Southern Services, Inc.

Chromatographic Analyses

GPC and HPLC were performed on a Waters ALC/GPC 202 high pressure liquid chromatograph equipped with a differential refractometer and a Schoeffel Spectroflow SF 770 variable wavelength ultraviolet-visible detector. For dual wavelength analyses, an Altex Model 153 Analytical UV Detector was used with a 254 nm filter. All chromatographic solvents were prefiltered through a 0.2 μ m Fluoropore filter before use.

GPC was performed using three μ -styragel columns, sizes 500 \AA , 100 \AA , 100 \AA , in series with tetrahydrofuran (UV grade, Burdick and Jackson) as mobile phase. Injection volumes and effective concentrations for analytical separations and for preparative analysis were 10 μ l at 10 mg/ml and 100 μ l at 50 mg/ml, respectively. Polyethylene glycol standards of molecular weights 285-315, 380-415, 570-670, 950-1050 and 3000-3700 from Union Carbide, and various polynuclear aromatics were used as calibration standards.

HPLC was performed for each of the six fractions obtained from GPC analysis. Reverse phase chromatography was employed for fractions 5 and 6 using two μ -Bondapak C₁₈ columns (30 cm long, 4 mm in diameter) with a mobile phase of equal volume portions of acetonitrile (nanograde, Mallinckrodt), 2-propanol (spectroquality, J.T. Baker) and water (glass-distilled). Ultraviolet detection, set at 254 nm and

0.1 AUFS, monitored the sample.

Fractions 1-4 were separated by normal phase chromatography employing a μ -porasil column (30 cm in length and 4 mm diameter) and a two-component mobile phase of hexane and 2-propanol. Isocratic solvent systems ranging from 100% hexane to 75% hexane/25% 2-propanol were used to effect a separation.

Gas chromatographic analysis of fractions 5 and 6 was performed on a Varian Model 1800 GC equipped with a flame ionization detector (FID) with nitrogen as the carrier gas. A Varian Model 3700 GC equipped with a flame photometric detector (FPD) with helium as the carrier gas was used for sulfur compound analysis. In both analyses, temperature programming and a methyl phenyl silicon column (10 feet by 1/8 inch) were used.

Analytical Methods Used in Fractional Analysis

Elemental analysis was performed on a Perkin Elmer Model 240 Elemental Analyzer equipped with a Microbalance and a Model 31 Tektronix Calculator. Samples were prepared by open-air evaporation of the THF from each fractional residue.

Fluorescence spectroscopy was performed on a Farrand Mark I Fluorescence Spectrometer with a standard quartz sample cell. Sample preparation consisted of dissolving each fraction in THF at concentration levels ranging from 1 to 10 mg/ml.

Infrared spectroscopy for fractions 1-4 was performed on a Digilab FTS 10 System I Fourier Transform infrared spectrometer (FTIR) and fraction 5 on a Perkin-Elmer 621 infrared spectrometer. Fractions 1-4 were run as KBr pellets and fraction 5 as a thin film.

Mass spectral analysis was performed on approximately 100 mg of each fraction with a Dupont Model 21-491 Mass Spectrometer equipped for solid sampling.

Ultraviolet spectroscopy was performed on a Cary 17 UV/Vis Recording Spectrometer using a standard 1 cm path length quartz cell and UV grade THF as solvent.

Results and Discussion

In this study, GPC is used as a method for the characterization of four SRC's and their respective feed coals, as well as a means of preliminary separation for the SRC's. The molecular size distributions of the tetrahydrofuran soluble portion of Amax, Illinois #6, Western Kentucky 9/14 and Monterey SRC's as determined by GPC is shown in Figure 1. The molecular size distributions of Western Kentucky SRC and Monterey SRC have higher molecular weight distributions than those of Illinois #6 and Amax SRC.

A comparison of the molecular size distributions of the THF soluble portion of SRC to the THF soluble portion of the feed coals is also shown in Figure 1. A large difference in the relative solubility of SRC and the feed coal is observed (See Table 1). The differences in the molecular weight distributions of the coals and SRC's are portrayed by their initial and final elution times as shown in Table 2. Two SRC's, Amax and Illinois #6, and one coal, Amax, show substantial differences in elution time. Both SRC's are delayed in initial elution time and continue past the experimental elution time for the smallest aromatic compound, benzene. The final elution time of Amax coal is also delayed - 33.0 minutes - compared to approximately 30.0 minutes for the other coals. These increased elution times can be attributed to partial adsorption of the components on the μ -styragel columns.

GPC Fractional Analysis

To analyze the chemical nature of solvent refined coal, the SRC must first be subdivided into smaller analyzable fractions. To accomplish this, the GPC eluent of Amax SRC was arbitrarily divided into six fractions. These fractions were collected at three minute intervals beginning at approximately 15.5 minutes, where the SRC eluent was first detected by the differential refractometer. The elution times of the Amax SRC fractions are compared in Figure 2 to the elution times of calibration standards and to known SRC asphaltene and oil fractions from Soxhlet extractions. The elution times from an autoclave reaction mixture, which most

closely approximates SRC process conditions, show that asphaltenes elute between 15.5 and 26.6 minutes and that the oil elutes between 23.6 and 32.2 minutes. Therefore, according to their elution times, Amax SRC GPC fractions 1-3 primarily consist of asphaltenes*, fraction 4 is a combination of oil compounds and asphaltenes, and fractions 5 and 6 are primarily composed of the oil fraction consisting of small condensed ring systems. (6)

Mass Spectrometry

Each GPC fraction was analyzed by electron impact mass spectrometry. The largest m/e value obtained for each fraction as shown in Table 3 is essentially limited by the volatility of each fraction at the maximum probe temperature 3000°C. This fact is exemplified by the nearly equivalent m/e values obtained for Amax SRC and GPC fraction 5 - 579 and 580 respectively. Residues remained on the mass spectrometer probe from each fraction and SRC sample indicating that only a portion of each sample was analyzed. Since all of the fractions, including the two oil fractions 5 and 6, have high molecular weight compounds, the GPC fractions of Amax SRC cannot be easily correlated to a molecular weight separation.

The mass spectral fragmentation pattern of fractions 1 and 5 are shown in Figure 3. These fragmentation patterns clearly illustrate the substantial differences in the chemical compositions of the GPC fractions. The fragmentation pattern of fraction 1 has mass peaks covering the entire mass range while fraction 5 has an intense cluster of mass peaks resembling a Gaussian distribution between mass number 150 to 400. The fragmentation pattern of fraction 2 closely resembles that of fraction 1; whereas, the fragmentation pattern 4 is similar to fraction 5. The fragmentation patterns of fractions 3 and 6 are both weak and sparse. These fragmentation patterns give an indication of the compounds composing the fractions. Fractions 1 and 2 contain easily fragmented compounds - such as heteroatom-containing aromatics or substituted aromatics. The concentrated Gaussian distribution of mass peaks in fractions 4 and 5 appears to be a true distribution of the molecular ions of the compounds present in the fractions, suggesting that these fractions contain compounds which give strong parent peaks and which do not easily fragment such as polynuclear condensed ring aromatics.

Fluorescence and Ultraviolet Spectroscopy

The fluorescence emission spectra of fractions 3, 4, and 5 are shown in Figure 4. The apparent fluorescence maxima for the three fractions range from 434 nm to 450 nm and the fluorescence bandwidths at half-height range from 144 to 168 nm. These values correspond to the apparent wavelength maxima and bandwidths of various polynuclear aromatics and coals as described by Retcofsky (7). Retcofsky and co-workers have shown that the apparent fluorescence wavelength maxima for polynuclear aromatic compounds of three or more condensed rings range from 383 to 482 nm. Retcofsky reports that the pyridine extracts from 5 coals have an apparent wavelength maxima ranging from 390 to 455 nm (with four of the coals ranging from 440-455 nm) and have an apparent bandwidth at half-intensity between 120-140 nm. Comparison of the apparent emission maxima and bandwidth of the SRC fractions (see Figure 4) to the fluorescence of the coals and standard polynuclear compounds gives strong evidence that the types of compounds present in fractions 3, 4 and 5 are polynuclear aromatic compounds of three or more condensed rings.

Ultraviolet spectroscopy of the Amax SRC GPC fractions compared to Amax SRC (THF soluble portion) and recycle oil show (Figure 5) considerable variation in the band structure. The UV spectra of fraction 1 shows definite band structure at 217, 243, and 262 nm; fraction 2 has absorption bands at 218, 242 and 264 nm. Fractions 3, 4, 5 and 6 show no band structure. The absorption bands of Amax SRC - 217, 241 and 261 nm - are very similar to fractions 1 and 2. In contrast,

* Preasphaltenes are not considered due to their insolubility in THF.

the numerous absorption bands of light recycle oil are shifted to longer wavelengths - 272, 278, 283, 285, 319 and 336 nm. This shift agrees with the fact that the oil is composed essentially of condensed polynuclear aromatic compounds of 2, 3, and 4 rings (6). The band structure in fractions 1 and 2 and Amax SRC is obviously due to a prominent functional group present in these samples but absent or in much lower concentration in the other GPC fractions and light recycle oil.

Elemental Analysis and Infrared Spectroscopy

Elemental analysis performed on each GPC fraction indicates considerable variation in the carbon and nitrogen percentages (see Table 4). Fractions 1-3 have a significantly lower carbon percentage than do fractions 4 and 5. In contrast, the percentage of nitrogen is definitely higher in fractions 1 and 2 as compared to fractions 4 and 5. The hydrogen values vary among the different fractions but not in any predictable fashion.

Infrared analysis of Amax GPC fractions 1-5 shows distinctive differences in the aliphatic band stretches, CH_2 at 2920 cm^{-1} and CH_3 at 2960 cm^{-1} , and the aromatic CH stretch at $3000\text{--}3100\text{ cm}^{-1}$. Table 5 shows the ratio of the aromatic C-H to the aliphatic CH_2 stretch and the ratio of CH_3 to CH_2 stretch for the Amax GPC fractions. Information concerning the types of compounds present in these fractions can be obtained from the ratios of the band stretches. With increasing elution time, GPC fractions 1-5 show increased aromaticity. A substantial increase in the CH/CH_2 ratio is seen in fraction 5. The CH_3/CH_2 ratio increases in fractions 1-3 and levels off at fraction 4; however, fraction 5 shows a dramatic increase in the CH_3/CH_2 ratio. These ratios along with the elemental analysis (see Table 4) give strong evidence that fractions 1 and 2 have either more heteroatoms or less aromatic compounds than do fractions 3, 4, and 5. Fractions 1 and 2 also have a greater percentage of methylene groups indicating that they have either longer hydrocarbon chains or more saturated cyclic groups in comparison to the other fractions. Fractions 3 and 4 have increased aromatic structure and shorter side-chains or fewer saturated cyclic compounds than 1 and 2. The large change in both the aromatic/ CH_2 and the CH_3/CH_2 ratios show that fraction 5 is totally different from the other fractions. Fraction 5 is largely aromatic with more methyl than methylene groups.

HPLC and GC Chromatographic Analysis of GPC Fractions

The Amax SRC GPC fractions are further separated by HPLC and GC into their component species (fractions 5 and 6) or into chromatographic bands (fractions 1-4). Since the elution times of fractions 5 and 6 correspond to that of oil and since both 5 and 6 are soluble in the reverse phase solvents, reverse phase affinity mode separations are successfully used.

As shown in Figure 6a, fraction 6 is separated into 30 peaks - some only partially resolved - by reverse phase HPLC. Several peaks in fraction 6 have been tentatively identified by spiking; they are: naphthalene, phenanthrene, fluoranthene, and pyrene. GC analysis of fraction 6 shows one major peak, identified by spiking as pyrene. Several other peaks - phenanthrene, fluoranthene and dibenzothiophene - have been identified by spiking as shown in Figure 6b.

Reverse phase HPLC separates fraction 5 into 35 peaks (see Figure 6c). There are more peaks present in fraction 5 than in fraction 6. At the same total concentration level the UV absorption of the chromatographic peaks is much greater in 5 than in 6. The gas chromatogram of fraction 5 shown in Figure 6d shows three major peaks which have been identified by spiking as phenanthrene, fluoranthene and pyrene. Fourteen intermediate and minor peaks are also present. Two of these components - dibenzothiophene and chrysene - have been identified.

The components identified in fractions 5 and 6 are essentially all 2, 3, and 4 condensed ring polynuclear aromatic compounds with one heteroaromatic sulfur species. Many of the compounds present in fractions 5 and 6 are also present in recycle oil (8). The origin of some of these polynuclear aromatic compounds in the final SRC product

can be attributed to one of two sources: 1) these compounds may be residual recycle oil which is not completely distilled or 2) these compounds may be an integral portion of the SRC organic matrix.

Normal phase HPLC separations of fractions 1-4 have been attempted since reverse phase HPLC is totally unsuccessful due to the lack of solubility of fractions 1-4 in reverse phase solvents. Analytical separations of fractions 1-4 are difficult due to their insolubility in many solvents; however, some progress has been made as shown in Table 6. Under normal phase conditions with a mobile phase of hexane (95%) and 2-propanol (5%), no bands in fraction 1 and 2 elute before 20 column volumes. With the same solvent system fractions 3 and 4 show some resolution into peaks and chromatographic bands at $k' < 20$. When a more polar mobile phase is used - hexane (75%)/2-propanol (25%), all the components in fractions 3 and 4 elute as a single band while fractions 1 and 2 elute as two broad bands in less than four column volumes. Under both mobile phases, condensed ring standards - such as phenanthrene, anthracene, dibenzothiophene and rubrene - all elute at the void volume of the column. Considering the mobile phase necessary to effect a separation, fractions 1 and 2 appear to have a composition quite different from fractions 3 and 4. Fractions 1 and 2 appear to be composed of polar compounds or condensed ring systems with high molecular weights; while fractions 3 and 4 appear to be composed of more non-polar but high molecular weight compounds.

Conclusions

GPC clearly shows that the molecular weight distribution of SRC is consistent with SRC being partially composed of oil and asphaltenes. The fractions, collected from the GPC elution of Amax SRC, are fairly well-defined: fractions 1-3 are composed of asphaltenes, fraction 4 is a combination of oil and asphaltenes, and fractions 5 and 6 are oil. The major constituents of fractions 5 and 6 have been identified as mainly three or four condensed ring polynuclear aromatics; fraction 6 contains primarily pyrene and fraction 5 contains three major components - phenanthrene, fluoranthene and pyrene. From the experimental evidence, fractions 1-4 can be characterized by their bonding type and chromatographic behavior. Fractions 1 and 2 appear to be somewhat polar, high molecular weight compounds dominated by chain structure possibly within an aromatic framework, while fractions 3 and 4 seem to be fairly high molecular weight but essentially non-polar compounds with a more prominent aromatic structure. Future HPLC work is planned to effect more complete separations of the components in fractions 1-4 for subsequent compound identification.

References

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TABLE 1. Solubility of Amax SRC and Four Demineralized Feed Coals in Tetrahydrofuran

<u>Material</u>	<u>Percent Soluble in THF*</u>
Amax SRC	86.65
Amax Coal	8.75
Monterey Coal	5.02
Western Kentucky Coal	3.88
Illinois #6 Coal	1.60

*Concentration level: 100 mg/ml

TABLE 2. Comparison of Elution Time for Solvent Refined Coals and their Feed Coals

	<u>Elution Time (minutes)</u>	
<u>SRC</u>	<u>Initial</u>	<u>Final</u>
Amax	24.40	46.75
Monterey	16.25	31.75
Illinois #6	21.90	43.25
Western Kentucky	15.50	29.75
<u>Feed Coals</u>		
Amax	15.75	33.00
Monterey	16.00	30.35
Illinois #6	15.90	30.48
Western Kentucky	15.00	28.75

TABLE 3. Highest Mass Spectral for Amax SRC Fractions and Amax SRC

<u>Fractions</u>	<u>m/e*</u>
1	650
2	640
3	370
4	680
5	580
6	658
Amax SRC	579
Asphaltenes (Amax Coal)	693

Probe temperature: 300°C
Ionizing voltage: 1400 V

TABLE 4. Elemental Analysis of Amax GPC Fractions and Amax SRC

<u>GPC Fractions</u>	<u>% C</u>	<u>% H</u>	<u>% N</u>
1	81.25	5.24	1.69
2	79.12	5.80	1.38
3	80.30	6.26	1.68
4	82.98	4.40	1.27
5	84.55	6.58	0.75
Amax SRC (THF insoluble portion)	84.18	4.64	1.60
Amax SRC	86.07	5.17	1.52
Recycle Oil	89.22	8.44	0.85

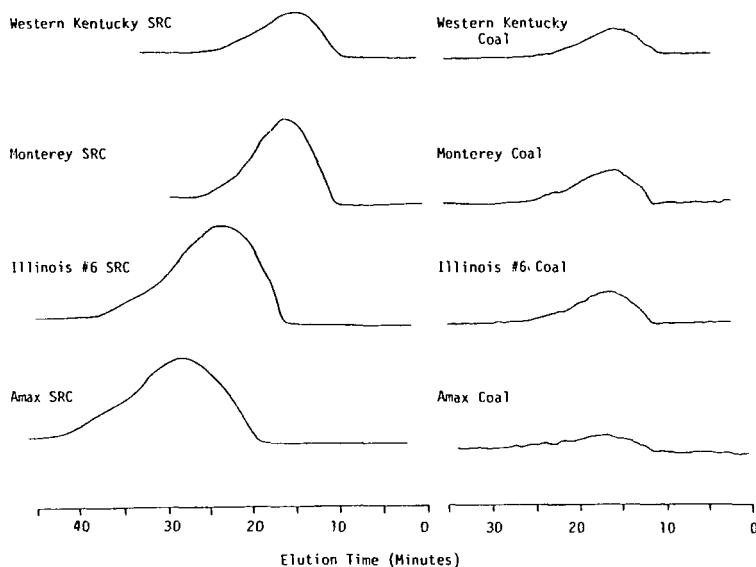
TABLE 5. Infrared Ratios of Amax SRC GPC Fractions

<u>Fractions</u>	<u>Ratios</u>	
	<u>Aromatic/Aliphatic (CH/CH₂)</u>	<u>Methyl/Methylene (CH₃/CH₂)</u>
1	0.077	0.79
2	0.151	0.81
3	0.201	0.92
4	0.298	0.88
5	0.837	1.28

TABLE 6. Normal Phase HPLC Analysis of Fraction 1-4

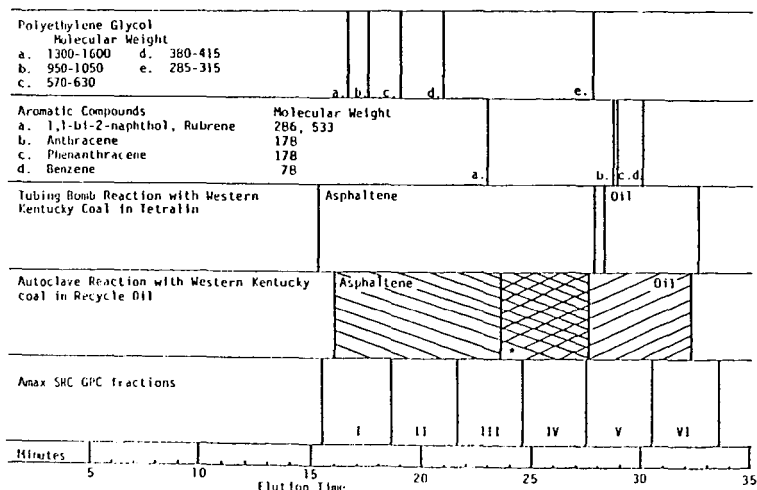
<u>Fraction</u>	<u>Mobile Phase</u>	
	<u>Hexane (95%)/2-Propanol (5%)</u>	<u>Hexane (75%)/2-Propanol (25%)</u>
1	No bands to $k' = 20$	Two broad bands, $1 < k' < 4$
2	No bands to $k' = 20$	Two broad bands, $0 = k' < 1.8$
3	13 peaks (poorly resolved) $k' < 20$	Single broad band, $k' = 0$
4	3 bands, $0 < k' < 1$	Single band, $k' = 0$

Figure 1. GPC^a of the SRC's and the Feed Coals^b



- a. UV detection at 300 nm
b. Coals demineralized (ASTM)

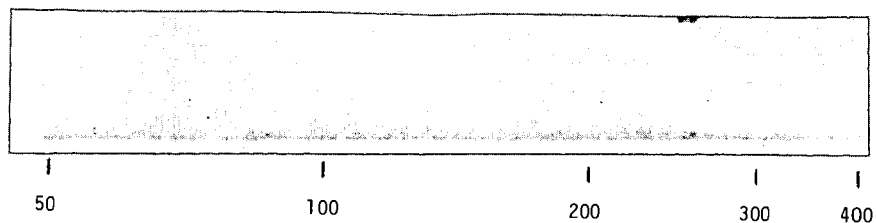
Figure 2. Comparison of the Elution Times of Amax SRC GPC Fractions to Known Standards



*Overlapped peak includes both asphaltene and oil fractions.

Figure 3. Mass Spectra of Two Amax SRC
GPC Fractions

Fraction 1



Fraction 5

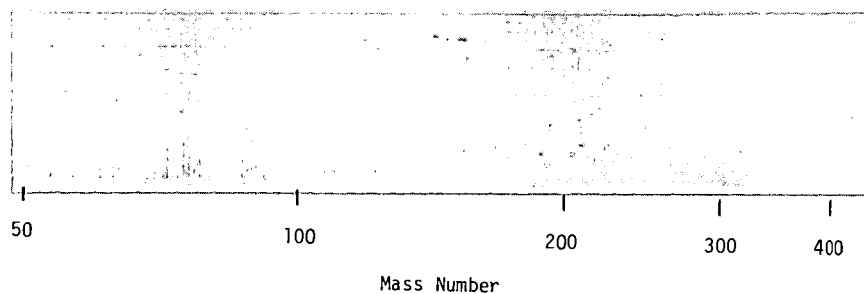
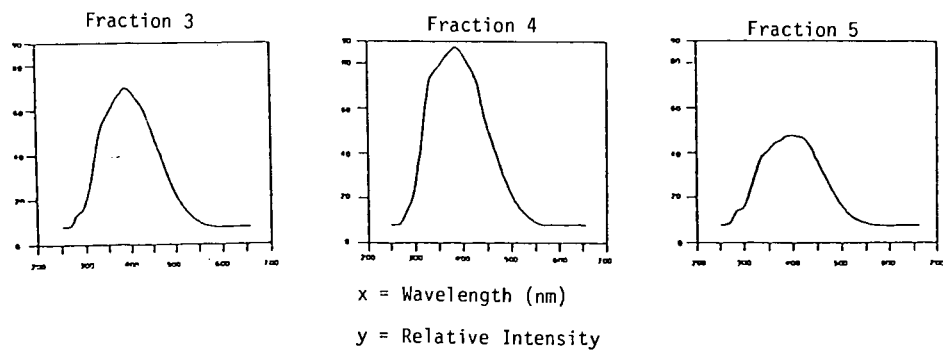


Figure 4. Fluorescence Spectra^a of Three Amax SRC GPC Fractions



a) Uncorrected emission spectra

Figure 5. Ultraviolet Spectra of Amax SRC,
Light Recycle Oil and Amax SRC
GPC Fractions

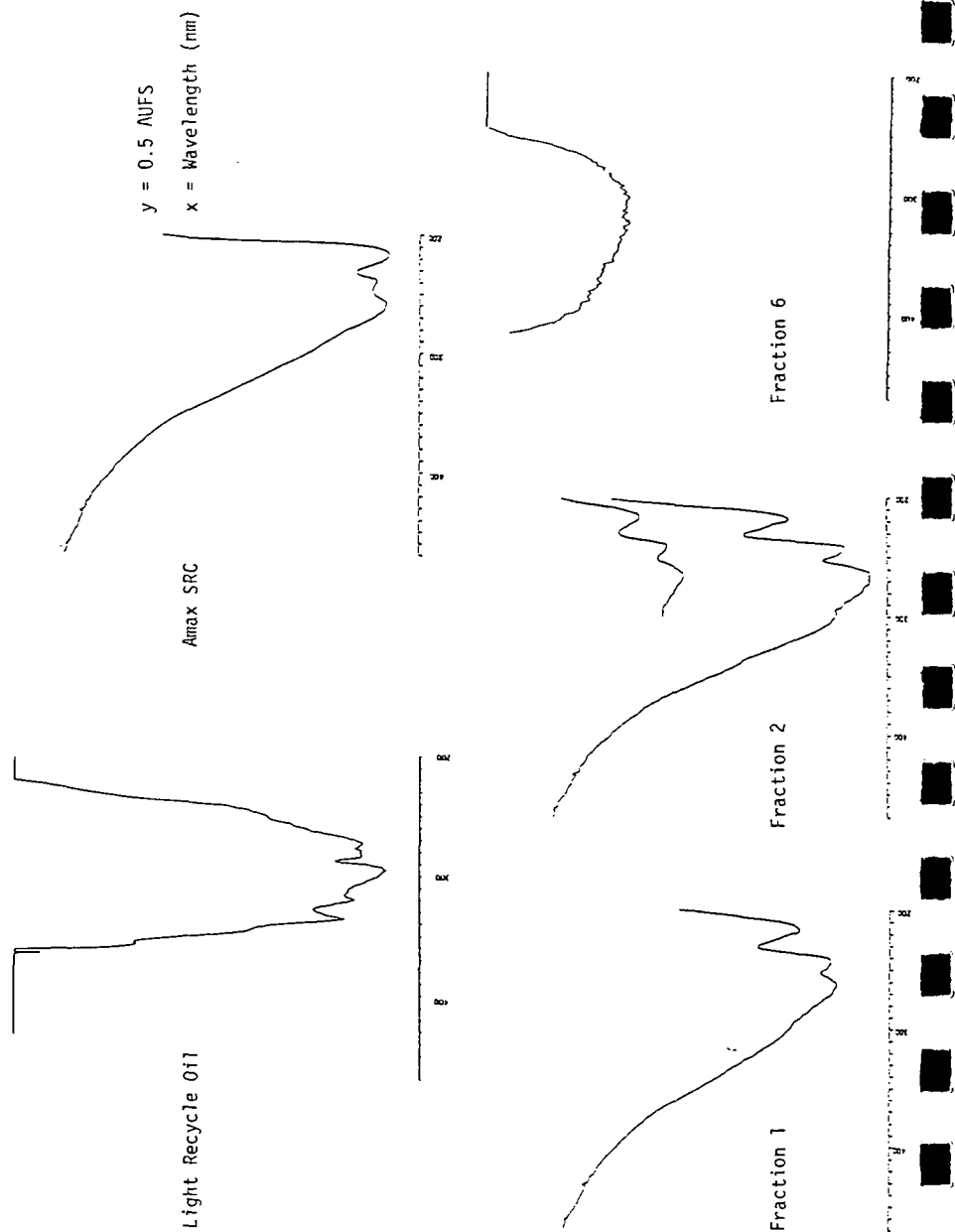
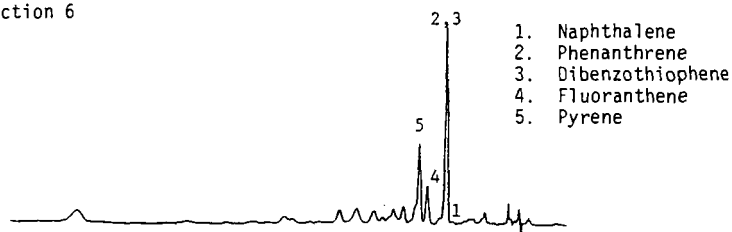
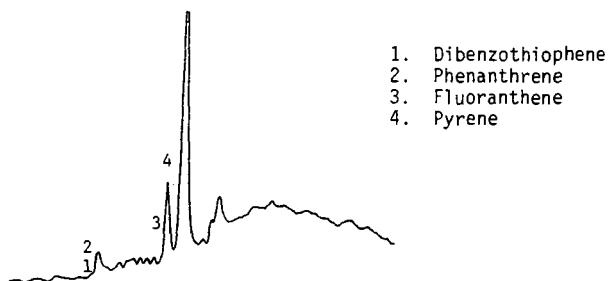


Figure 6. Liquid and Gas Chromatograms of Fractions 5 and 6

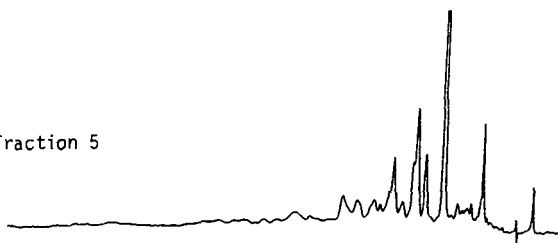
a) HPLC of Fraction 6



b) GC of Fraction 6



c) HPLC of Fraction 5



d) GC of Fraction 5

